

# Prospective applications of renewable energy based electrochemical systems in wastewater treatment: A review

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## ABSTRACT

Recent decades are characterized by incredible rapid technological development resulting in the introducing of various new chemicals, materials and processes with various complexities. This, in turn, is associated with release of increased amounts of pollutants into the environment and for this reason their efficient removal is required. Environmental monitoring results show that many pollutants in ground water are at the excess limit which raises concerns on currently employed wastewater treatments. This review summarizes the electrochemical technology used in wastewater treatment covering its advantages such as high removal efficiency, clean energy conversion, low environmental impact, easy operation and compact design. Significant enhancement of electrochemical methods such as electrocoagulation, electroflootation, electrooxidation, electroreduction and electrodisinfection is discussed and these technologies are combined with an advanced photovoltaic (PV) technology. Important design parameters to obtain the highest efficiency from this combined technology are discussed in details. Moreover, it is shown that the combination systems are capable to produce hydrogen gas at high efficiency which can be used as a supplementary source for green energy thus minimizing the entire process cost.

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## 1. Introduction

Groundwater is the most important source of drinking water. According to the United States Environmental Protection Agency, groundwater is seriously polluted by many human activities such as landfills, agricultural byproducts, mining, septic systems, oil, gas and industrial injection wells [1]. The major contaminants discharged by these activities are arsenic (As), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), zinc (Zn), selenium (Se), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), phenolic compounds and total dissolved solids (TDS) [2]. Large numbers of environmental pollutants are found at the levels exceeding the permissible concentrations which pose a serious threat on the efficiency of wastewater treatment technologies currently used.

Many research studies are dedicated to investigate various aspects of the wastewater treatment technologies and it is found that waste pollutants can be removed as well as treated by different methods. The conventional methods to remove solid particles from wastewater are sedimentation, flotation, filtration, coagulation and flocculation. For the elimination of organic and inorganic compounds biological treatment, advanced oxidation, adsorption and membrane process are more appropriate [3–6]. The conventional methods of water treatment are effective but they have some drawbacks such as production of large volumes of sludge, requirement of high energy, problems associated with fouling and generation of huge byproducts [7].

In the past two decades, more advanced electrochemical methods have been introduced and widely used in water treatment area. The advantages of the electrochemical treatment include high removal efficiency, clean energy conversion, pollution avoidance due to no emissions generation, easy operation and compact facilities [8,9]. Electrochemical methods include electrocoagulation, electroflootation, electrooxidation, electrodisinfection and electroreduction processes which are discussed further. This review mainly focuses on the application of electrochemical methods in water and wastewater treatment processes powered by solar energy based photovoltaic technology. The discussion provides an opportunity to expand the boundaries of conventional electrochemical system towards higher sustainability and reveals unlimited future prospects for multiple purposes.

## 2. Electrochemical treatment

### 2.1. Electrocoagulation

Electrocoagulation process generates coagulants by an in situ process when electric current is passed through aluminum or iron anode which releases metal ions into a solution. The reaction is summarized in Eqs. (1) and (2). The as-synthesized metal ions further react to produce hydroxides, polyhydroxides and polyhydroxy-metallic compounds which have strong affinity towards the oppositely charged ions present in solution to stimulate the coagulation process. Hydrogen is generated at the cathode and it can be recovered for use as an energy source or a reactant for other industrial applications [10]. The formed flocs have large surface area which is capable to adsorb soluble organic compounds and to trap colloidal particles present in the solution. The accumulated flocs are removed by sedimentation or flotation process [11]. Table 1 shows a set of anodic reactions occurring at acidic and alkaline conditions. Some researchers demonstrated that alkaline solution is more suitable

for iron anode, whereas neutral or weak acidic solution is effective for aluminum anode in COD (chemical oxygen demand) removal process [12,13]. The benefits of electrocoagulation include generation of reactive coagulant by an in-situ process and having compact equipment setup [14]. However, large-scale installation of electrocoagulation system is rare and can be found only a few numbers worldwide [10]. Table 2 presents the efficiencies of electrocoagulation method in treating different types of wastewater. It is reported that electrocoagulation system has been successfully used in wastewater treatment of tannery, textile, oil, fertilizer, dairy and metal processing industries [12,13,15–19]. Reaction of iron ions and peroxide hydroxide to form Fenton's reagent is discussed in the electrooxidation section.



### 2.2. Electroflootation

Flootation technique is widely used to recover fine mineral particles, de-inking of recycled paper and to separate oil from water [20]. The recovery of particles (diameter: 1–10 μm) is inversely proportional to the bubble size. In conventional methods to generate bubbles such as agitated and sparged columns is too large [21]. Smaller and homogeneous gas bubbles of hydrogen and oxygen can be produced at the electrodes surface under the applied electric current in electroflootation process. Moreover, the concentration of gas bubbles can be controlled by varying the current density. Increased current density promotes collision among the bubbles, particles and oil drops which in turn affect the concentration of bubbles [22]. Electrode material and pH are the most significant parameters to control the bubble size and their distribution. It is reported that smallest hydrogen bubbles can be obtained at neutral pH; whereas oxygen bubbles size increases with pH [23]. Electroflootation is very efficient for separating oil from water or oil emulsions, textile and heavy metal as it is shown in Table 2.

Some researchers combined both electrocoagulation and electroflootation processes into a single system to treat various types of wastewater. Electrocoagulation occurs at the anodic side, where aluminum or iron anode dissolves to produce coagulant ions of Al<sup>3+</sup> or Fe<sup>2+</sup>; while hydrogen evolves at the cathode side thus inducing the flotation process [24]. Current density is the most important parameter in such combined system since the dissolution of anode, generation of bubbles and size of the bubbles increase with increasing the current density [25]. Electrolyte conductivity, electrode arrangement and pH are the other influencing parameters of the combined system. Some experimental results of such combined system for treating textile and heavy metal containing wastewater and river water is tabulated in Table 2.

**Table 1**  
Chemical reactions with different anode materials at acidic and alkaline conditions [9].

Condition	Anode material	Anode reaction	Cathode reaction
Alkaline	Aluminum	$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
	Iron	$\text{Fe}^{2+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$	
Acidic	Aluminum	$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$	
	Iron	$4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + \text{OH}^-$	

**Table 2**

Efficiency of different wastewater treatment by different electrochemical type.

Electrochemical type	Effluent source	Electrode material	Experimental conditions	Removal efficiency (%)	Ref.
Electrocoagulation	Olive oil mill	Anode (A): Al Cathode (C): Fe	Voltage: 12 V Current Density Current density (CD): 20 mA cm <sup>-2</sup> pH: 6 ± 0.2 Duration: 10 min Temp: 21–22 °C Initial COD: 48500 mg/L Initial color: 2120 m <sup>-1</sup> String speed: 200 rpm Temp: 25 ± 0.1 °C PAC: 0.8 kg/m <sup>3</sup> Duration: 10 min Initial COD: 3422 mg/L	COD: ~50 Color: 95	[12]
	Dyeing solution containing polyaluminium chloride (PAC)	A: Al C: Al	String speed: 200 rpm Temp: 25 ± 0.1 °C PAC: 0.8 kg/m <sup>3</sup> Duration: 10 min Initial COD: 3422 mg/L	COD: 80	[13]
Tannery		A: Al C: Al A: mild steel C: mild steel	Stirring speed: 150 rpm Current: 1 A Duration: 60 min	COD: ~50 TOC: ~50 Sulfide: ~17 Nitrate: ~32 COD: ~52 TOC: ~40 Sulfide: ~17 Nitrate: ~31	[15]
Dairy production		A: Al C: Al	Temp: room temp Stirring speed: 500 rpm CD: 0.43 A/dm <sup>2</sup> Duration: 30 min Initial dissolved milk: 2.5–20 g/L	COD: 61 Phosphorus: 89 Nitrogen: 81 Turbidity: 100	[16]
Synthetic wastewater: Cu(4mg/L), Cd (12mg/L) and Pb (4mg/L)		A: Steel sheet C: Steel sheet	CD: 36 A/m <sup>2</sup> Duration: 10 min Temp: 20 °C Batch mode Conductivity: 1100mS/cm pH:7–9	Copper: 100 Cadmium: 100 Lead: 100	[17]
Synthetic water		A: Fe C: Fe	Initial NO <sup>3-</sup> -N: 25 mg/dm <sup>3</sup> CD: 1 mA/cm <sup>2</sup> Fe molar concentration: 100 mmol/dm <sup>3</sup>	NO <sup>3-</sup> -N: 92	[18]
Leachate from Yanqun landfill, China		A: Fe C: Fe	Batch mode Stirring: 200 rpm Duration: 90 min CD: 4.96 mA/cm <sup>2</sup> Cl <sup>-</sup> : 2319 mg/L	COD: 49.8 NH <sub>3</sub> -N: 38.6 Total phosphorus: 82.2 BOD <sub>5</sub> : 84.4 Turbidity: 69.7	[19]
Electroflootation	Apple juice with 200 mg/L gelatin 50 mg/L crude oil mixed with water	A: Graphite rod C: Ss screen A: Al plate perforated uniform with 2 mm C: Al plate perforated uniform with 2mm A: Al C: Al	CD: 20 mA/cm <sup>2</sup> Duration: 30 min Batch mode 5 V 0.4 A Duration: 30 min pH: 4.72 Duration: 20 min Voltage: 20 V pH: 7.98 k: 3.12 mS/cm	Turbidity: 3.4 NTU Oil: 90	[22] [87]
Velvet manufacturing wastewater	Synthetic wastewater containing heavy metals		Duration: 20 min Voltage: 20 V pH: 8 k: 2.7 mS/cm	BOD <sub>5</sub> : 93.5 COD: 90.3 SS: 93.3 Turbidity: 78.8 Color: 92.5 Fe: ~97.5 Ni: ~80 Cu: ~96 Zn: ~99 Cd: ~95 Pb: ~97	[88]
	Synthetic wastewater (copper sulfate mixed with tap water)	A: Ru/Ti plate C: Ss screen	pH: 6 Current: 300 mA Temp: 20 °C Duration: 60 min Sodium sulfate: 1 g/L Copper conc.: 100 mg/L	Cu: ~92	[89]
Combination of electrocoagulation and electroflootation	Textile w/w	A: Al sheet C: Al perforated sheet	Room temp CD: 11.55 mA/cm <sup>2</sup> Retention time (RT): 10 min pH: 8.7 k: 4.571 ms/cm	BOD <sub>5</sub> : 83.05 COD: 68 SS: 86.51 Turbidity: 81.57 Color: 92.5	[25]

**Table 2** (continued)

Electrochemical type	Effluent source	Electrode material	Experimental conditions	Removal efficiency (%)	Ref.
	Synthetic heavy metal w/w (CuSO <sub>4</sub> ·5H <sub>2</sub> O, NiSO <sub>4</sub> ·6H <sub>2</sub> O, ZnSO <sub>4</sub> ·7H <sub>2</sub> O, CdSO <sub>4</sub> ·8H <sub>2</sub> O, PbSO <sub>4</sub> )		pH: 7.5–7.8 k: 2.4mS/cm Temp: 20 °C CD: 11.55 mA/cm <sup>2</sup> RT: 30 min	Cu: ~98.2 Ni: ~99.5 Zn: ~98.7 Cd: 98.5 Pb: 100	[25]
Laundry		A: Ti C: Ti	pH: 7 HRT: 10 min I: 1.2A PAM: 1 mg/L pH: 7.5 Initial COD: 226 mg/dm <sup>3</sup> Voltage: 5V	COD: ~78 MBAS: ~95 Phosphate: ~98 Turbidity: ~99	[90]
Laundry		A: Al plate C: Al plate		COD: 62	[24]
River water		A: Al plate C: Al plate	Temp: 17 °C pH: 7.6 k: 0.41 mS/cm	Chloride: 2 Total hardness: 21 Nitrate: 26 Phosphate: 99 TSS: 51	[91]

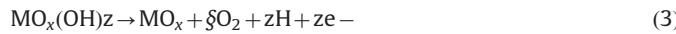
k: conductivity.

Ss: stainless steel.

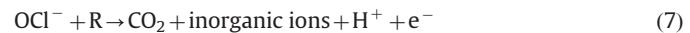
### 2.3. Electrooxidation

Electrooxidation can be divided into two parts: the direct anodic oxidation and indirect anodic oxidation. In the direct electrooxidation pollutants are directly oxidized at the anode surface through physical adsorption of hydroxyl radicals (·OH) or chemisorbed as “active oxygen” (MO<sub>x+1</sub>). Three main parameters affect this process: ability to generate physically or chemically adsorbed hydroxyl radicals; characteristics of anode material; and applied current to oxidize pollutants and oxygen evolution reaction [26].

Organic compounds are completely oxidized when exposed to hydroxyl radicals because the radicals are electrophiles and rapidly react with electron-rich organic compounds [27]. The chemisorbed “active oxygen” reacts with the pollutants at the dimensionally stable anodes such as, RuO<sub>2</sub> and IrO<sub>2</sub>. Oxygen is formed at the anode during the electrolysis of water and it is considered as a factor to decrease the efficiency of electrooxidation process. However, selection of anode material with higher over potential oxygen evolution is required to ensure the direct anodic oxidation is prioritized at high current density over the oxygen evolution [9]. Reactions depicted in Eqs. (3) and (4) also show that physically and chemically adsorbed hydroxyl radicals enhance the generation of oxygen [22]. For this reason, addition of oxidizing agents is recommended to increase the overall efficiency of oxidation.



Oxidizing agents such as chlorine, hypochlorite, Fenton's reagent, peroxodisulphate and ozone are usually used for indirect anodic oxidation process. Chlorine and hypochlorite are commonly utilized to eliminate oxidizable pollutants since oxide electrodes are very active for Cl<sub>2</sub> generation [8,28]. However, the common drawback of such agents is the formation of organic chlorinated intermediates (RCI) which are considered as mutagenic and carcinogenic byproducts [29,30]. The following reactions (Eqs. (5)–(8)) reflect the degradation mechanism of organic pollutants (R) by indirect anodic oxidation with chlorine [7]:



Another common oxidizing agent is Fenton's reagent which is a mixture of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferrous ion (Fe<sup>2+</sup>) which effectively reacts at pH level around 3. Electro-Fenton process has two phases: firstly, the Fenton's reagent is externally fed into a reactor containing high catalytic activity inert electrodes as an anode material; secondly, H<sub>2</sub>O<sub>2</sub> is added and Fe<sup>2+</sup> ions are supplied through oxidation of the iron anode. Electro-Fenton process is generally influenced by parameters such as pH, Fe/H<sub>2</sub>O<sub>2</sub> ratio, presence of other anions, chelating agent and humic substances [31,32]. This process is more eco-friendly and economically feasible compared to the conventional Fenton process. The degradation mechanism of organic pollutants (RH) in the electro-Fenton process is graphically explained in Fig. 1 [27,33].

### 2.4. Electroreduction

Like electrooxidation, the process electroreduction also can be divided into two groups: direct and indirect reduction processes. Direct reduction process is more popular for nitrate reduction, where electrons from the cathode surface react with nitrate compound to form nitrogen gas and hydroxyl ions [34]. However, some undesirable by-products such as nitrite and ammonia are also formed during nitrate electroreduction. These two by-products can be eliminated by redox reactions where nitrite is reduced to nitrogen at the cathodic side and ammonia is oxidized at the anodic side, as shown in Eqs. (9)–(11) [35,36].



Indirect electroreduction is popular for treating vat dye wastewater. Vat dye is insoluble in aqueous solution and their poor contact with the cathode surface restricts to carry out direct electroreduction process [37,38]. Therefore, soluble redox mediators such as anthraquinone, Fe-triethanolamine (FE-TEA) and glucose are employed to induce the indirect reduction process [38,39]. Fig. 2 presents indirect electroreduction of vat dye where strong reducing agents are used to oxidize the dye into soluble leuco-form. The reduced form of vat dye has affinity to cellulose

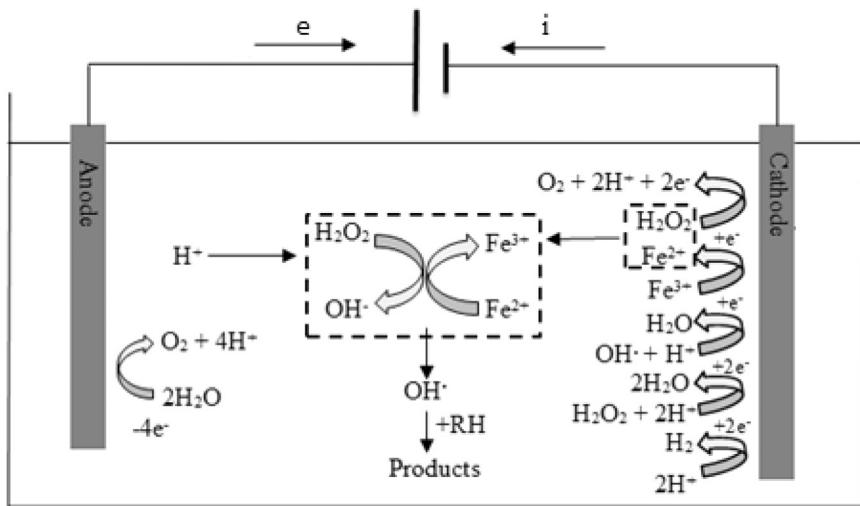


Fig. 1. Mechanism of organic pollutants oxidation by electro-Fenton process.

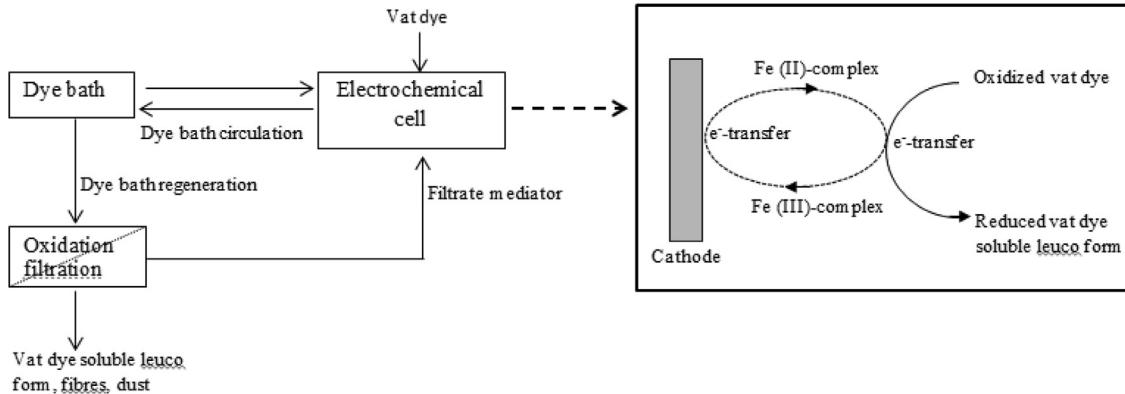


Fig. 2. Flow and reaction scheme of indirect electroreduction of vat dyes [37,40].

fibers and for this reason it is exhausted from dye bath. Then, the exhausted dye is re-oxidized into the original dye water which is the insoluble form of the fiber [40]. After reduction, the mediator is separated from soluble leuco dye by ultrafiltration which allows separating and recycling of water and mediator. However, indirect electrochemical vat dye reduction process is difficult to employ in industrial scale since the operating cost and profit are not attractive [37].

## 2.5. Electrochemical disinfection

Disinfection is a common water treatment process to eliminate various pathogenic microorganisms. Chlorination is the most popular method for water disinfection since the last century. But excessive presence of chlorine in water is associated with the generation of residual carcinogenic chloroform when natural organic matter (NOM) presence in the water [41]. Other disinfection methods such as ozonation, UV radiation and  $\text{ClO}_2$  oxidation are also effective, especially for getting instant disinfection results. However, these treatments are more expensive and the treatment efficiency starts to dissipate as soon as the process is finished. On the other hand, electrochemical disinfection has advantages such as elimination of a wide range of microorganisms, minimal chemical usage, no issues on their storage, easy operation and low

cost [42]. During electrochemical disinfection, water flows through a disinfectant equipped with electrodes charged with electric current [43]. Electrochemical disinfection setups can be classified into two types: direct electrolyzer and mixed oxidants generator. Direct electrolyzer produces oxidants directly from the contaminated water via electrolyzer; whereas mixed oxidants generator produces strong oxidizing species such as free chlorine, chlorine dioxide, hydrogen peroxide, ozone, and other short-live radicals from a supplied concentrated brine solution [44,45]. The active chlorine species such as  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{OCl}^-$  are the most common oxidants used in saline water.

It was demonstrated that reactive oxygen species ( $\text{OH}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2^-$ ) generated through water oxidation has higher disinfection efficiency compared to electro-chlorination efficiency [46]. Important parameters for electrochemical disinfection process are electrochemical cell configuration, electrode system, electrolyte composition, present of microorganism's species, flow rate and current density [42,44–46].

## 3. Electricity generated by renewable energy

According to the statistics from the International Energy Agency, electricity consumption for industrial, transportation,

agricultural, commercial, public and residential services increased from 439 to 1536 Mtoe (million tonnes of oil equivalent) since 1973 to 2010 in worldwide [47]. In industries a considerable portion of the generated electricity is used for wastewater treatment. Application of the electrochemical methods for wastewater treatment leads to increase electricity consumption and subsequent treatment cost, since current density is one of the important parameters in those processes. This in turn induced a vigorous ongoing search for new treatment approaches and alternative power sources by the industrial and research communities. According to the World Energy Forum, the fossil fuel resources will be exhausted in less than another 10 decades [48]. This fact adds pressure on the economy planners, policy makers and researchers to find efficient and renewable energy sources to replace the conventional ones to reduce human dependency on the oil and gas. Moreover, electricity generated by coal, oil, natural gas and nuclear power will increase the carbon dioxide emissions which is a cause for global warming.

The general renewable energy resources are geothermal, solar, wind, biomass and hydro. It is reported that electricity generation by using renewable energy has increased from 1321 to 4222 TWh (terawatt hour) since 1973 to 2010 in worldwide [47]. This proved that the renewable energy has a great potential to reduce the use of non-renewable sources for the generation of electricity in the near future. Out of these, solar energy is an attractive renewable energy source for the countries having tropical and subtropical climate where the annual average of solar irradiance is between 1000 kWh/m<sup>2</sup> and 2500 kWh/m<sup>2</sup> [49]. Solar energy is abundant, freely available, sustainable, free from greenhouse and toxic gases, and it allows immediate transmission electricity as well as storage [50]. Generation of electricity by using solar photovoltaic (PV) system has gained popularity in the recent years because of the capability to convert the sunlight into direct electric current without implying any threat to environmental. This source is well used in water pump, lamp, batteries chargers and supply electric utility grids. Earlier it was proved that PV system can produce power in all types of weather. In partly cloudy days, it is capable to produce up to 80% of their potential energy; on hazy or humid days it has approximate capacity of 50%; and extremely overcast days it is still capable to generate up to 30% of their potential energy [51]. The number of PV modules has significantly increased worldwide in the last decade which indicates the great potential of PV systems for present and future [52].

Generally, a PV system can be categorized into two types: stand-alone and grid-connected systems. A battery is required in the operational setup for stand-alone PV system and it is suitable for installation in rural areas. On the other hand, grid-connected PV system is linked to the local grid and generated solar electricity which is distributed through a local power provider [53,54]. Several financial incentives are offered to the public sector for the installation of the PV system in their premises with objectives to encourage people to use renewable energy sources and improve environmental awareness.

#### 4. Photovoltaic–electrochemical system

PV systems used as a power supply for electrochemical systems has been investigated and reported by only a few researchers. Some of them used textile wastewater as electrolyte solution since such wastewater is high in COD and contains different types of organic compounds which do not degrade during biological treatment. Azo dyes and their intermediates present in textile wastewater are toxic, carcinogenic and mutagenic [55]. Therefore, a hybrid PV-electrochemical process is designed for simultaneous removal of organic compounds and to generate hydrogen gas [56,57].

The fundamental components of a PV system are PV module, batteries, regulator or controller and inverter. Absorption of solar radiation by the surface of PV module transforms into electric energy (direct current). Then the electric energy is passed to a regulator before sending to batteries. The function of regulator is to prevent the batteries from overcharging or excessive discharge. The stored energy is used as backup electricity during low solar radiation and at night [58]. Dominguez-Ramos et al. (2010) reported that PV setup without battery results overall poor efficiency for water treatment due to the absence of backup electricity supply during the low solar radiation episodes. Beside this, without a battery the treatment process can be operated only daytime [59]. The role of inverter is to convert the direct current to alternating current (AC) for devices that work in AC mode [58].

##### 4.1. PV-electrochemical system design

Some important design parameters of PV-electrochemical system such as entropy generation, light absorbing material, PV array configuration, tilt angle, electrode materials, shape and arrangement have been investigated.

**Table 3**  
Irreversible analysis chemical reaction.

Chemical reaction	$v_A A + v_B B \rightarrow v_C C + v_D D$
	where $v_A$ , $v_B$ , $v_C$ and $v_D$ are stoichiometric coefficient of chemical reaction
Entropy variation within system, $\Delta S_{int}$	$\Delta S_{int} = \int_0^T \frac{A}{T} \frac{dx}{dt} dt$ with $A = -(v_A \mu_A + v_B \mu_B - v_C \mu_C - v_D \mu_D)$ $\mu_i = \mu_{i0}(T, p) + RT \ln\left(\frac{c_i}{c_{i0}}\right)$ $= f(T, p) + RT \ln(n_i)$ $A = -RT \left[ v_A \ln\left(\frac{n_A}{n_{A0}^{eq}}\right) + v_B \ln\left(\frac{n_B}{n_{B0}^{eq}}\right) - v_C \ln\left(\frac{n_C}{n_{C0}^{eq}}\right) - v_D \ln\left(\frac{n_D}{n_{D0}^{eq}}\right) \right]$ Hence, $\Delta S_{int} = -R \int_{\xi=0}^{\xi=0} \left[ v_A \ln\left(\frac{n_A}{n_A^{eq}}\right) + v_B \ln\left(\frac{n_B}{n_B^{eq}}\right) - v_C \ln\left(\frac{n_C}{n_C^{eq}}\right) - v_D \ln\left(\frac{n_D}{n_D^{eq}}\right) \right] d\xi$ where 0 means standard state, $p$ is the pressure, $c$ refers to the concentration, $f$ function non depending on the concentration, $R$ is the gas constant and $eq$ demonstrate chemical equilibrium.
Entropy exchange with environment, $\Delta S_{ext}$	$\Delta S_{ext} = \int_0^T \frac{Q}{T} dt$ where $Q$ is the heat power transfer between system and environment, $T$ refer to temperature
Entropy generation, $S_g$	$S_g = \Delta S_{int} + \Delta S_{ext}$ $= -R \int_{\xi=0}^{\xi=0} \left[ v_A \ln\left(\frac{n_A}{n_A^{eq}}\right) + v_B \ln\left(\frac{n_B}{n_B^{eq}}\right) - v_C \ln\left(\frac{n_C}{n_C^{eq}}\right) - v_D \ln\left(\frac{n_D}{n_D^{eq}}\right) \right] d\xi + \int_0^T \frac{Q}{T} dt$

#### 4.1.1. Entropy generation

Sun emits light carrying energy flow which transmits in disorder and fractal way. Entropy generation is used to evaluate an open system by related to their irreversibility. Irreversibility is a physical model to describe the thermodynamic phenomena and path in stochastic order. The entropy generation for photons from the Sun to the Earth is [60]:

$$S_{g,v} = \frac{h\nu N_v}{T} \ln \left( \frac{d_{SE} - R_S}{R_S} \right) \quad (12)$$

where  $h$  is the Planck's constant ( $6.626 \times 10^{-34}$ ),  $\nu$  depicted the frequency,  $N_v$  is the number of photons emitted from Sun,  $T$  is the temperature of Universe (2.7 K),  $d_{SE}$  related to distance between Sun and Earth ( $1.49 \times 10^{11}$  m) and  $R_S$  is the radius of Sun ( $6.96 \times 10^8$  m).

Lucia. U. (2013) had discussed the irreversible analysis chemical reaction by using entropy generation which illustrated in Table 3. This is linked to fluctuation of molecules number at equilibrium state [60]. High entropy generation caused lost energy in a process. The ideal condition of a system is to obtain a minimum entropy generation, which means that energy lost is minimum while the efficiency is maximum. However, entropy generation from the environment should be higher so more energy can be transferred from environment to the system [61].

#### 4.1.2. Light absorbing material

Light absorbing material is required in all solar cells to absorb photons and to produce electrical current carrier such as electrons and holes [59]. Crystalline silicon or silicon wafer is the dominant technology for manufacturing of PV solar cells. The monocrystalline silicon and polycrystalline silicon are popular for high efficiency solar cells. The advantages of silicon as light adsorbing material include its abundant presence in the earth's crust, non-toxicity, semiconducting nature and natural oxide properties, low segregation coefficient for many metals and easily doping for P- and N-type junctions. However, silicon is an indirect band gap semiconductor which requires thick active layer (1.5 mm) to absorb full solar spectrum [62]. Then application of amorphous silicon (a-Si) has attracted the attention of the researchers as it is a direct band gap semiconductor, and therefore, the thickness of the active layer is substantially smaller. Such attractive properties made this material the most popular in the Si thin film technology along with lower production cost. However, such apparent advantage of amorphous silicon is weakened by the lower efficiency and light degradation [63].

Cadmium telluride (CdTe) and cadmium sulfide (CdS) are promising materials for the manufacturing of thin film solar cells. The band gap of CdTe is 1.51 eV which is close to the solar spectrum for PV energy conversion [64]. This material enables the formation of a thin film and overcomes the short diffusion lengths of minority carriers. CdS normally transmits visible spectrum and is usually used as a window material for solar cells [65,66]. Other materials such as copper indium (gallium) diselenide (CIS/CIGS), dye sensitized solar cell and organic solar cell also investigated by a few researchers including the material's characteristics, solar cell configuration and fabrication process [52,67,68].

Table 4 presents reported solar cell efficiencies for different types of installations [69]. Crystalline silicon module showed the highest efficiency, while organic solar cell indicated the lowest efficiency which can be improved through further research in the future. Presently, majority of the light adsorbing material in PV modules in the world market is made from crystalline silicon module. However, the shortage of crystalline silicon has resulted in the increase of the manufacturing of thin film modules. This is because, the thin film modules require little or no silicon for their

**Table 4**  
Efficiency of different solar cell types [69].

Device	Standard product (%)	Commercial capacity (%)	Maximum laboratory efficiency (%)
Monocrystalline	13–20	23.4	25
Polycrystalline	11–16	17.3	20.3
Amorphous silicon (a-Si)	6–8	8.3	15.4
Cadmium telluride (CdTe)	8–10	10.9	16.5
Copper indium (gallium) diselenide (CIS/CIGS)	10–12	12.2	19.0
Dye sensitized solar cell	4–8	8	11.1
Organic solar cell	2–5	5	6.5

production and the overall production cost is lower compared to the crystalline silicon modules [70].

#### 4.1.3. PV array configuration

The arrangement of PV array influences the  $I$ - $V$  (current-voltage) curve: for PV modules connected in series, open circuit voltage ( $V_{oc, array}$ ) increases and short circuit current ( $I_{sc, array}$ ) remains constant in a single PV module,  $I_{sc}$ . Similarly,  $I_{sc, array}$  increases and  $V_{oc, array}$  remains the same in a single PV panel for the PV modules connected in parallel [71]. PV array configuration is the main factor to influence the power generation. The relationship among the parameters is shown in the following equations:

$$V_{oc, array} = NV_{oc} \quad (13)$$

$$I_{sc, array} = MI_{sc} \quad (14)$$

where  $N$  is the number of panels connected in series and  $M$  is the number of modules connected in parallel.

Valero et al. (2008) demonstrated that PV array in series arrangement is more suitable for the use in low conductive solutions whereas parallel arrangement is good for high conductive solutions to generate higher current intensity. It is important to make flexible configuration of the PV array arrangement so that it can allow reshaping according to the instantaneous solar irradiation fluctuations [58].

#### 4.1.4. Orientation and tilt angle

Orientation and tilt angle of solar panels is one of the main parameters to maximize the total amount of sun radiation on solar panel. In general, the solar panels are oriented toward equator. There are faced towards south in northern hemisphere and faced to the north in southern hemisphere. However, to obtain maximum solar radiation is more dependent on the tilt angle and it varies from location to location [72]. The optimum tilt angle is also affected by the latitude of the location and climate condition [73]. Some of the angle-latitude ( $\phi$ ) relations are summarized in Table 5 for determining the optimum tilt. These relations are more suitable for sunny climates where the sites lying in between 5°N and 40°N latitudes and having direct beam of radiation. The areas located beyond 45° N like Northern Europe possesses cloudier climate which causes the sun radiation to diffuse, so, the relations do not give precise results on it. However, most of the PV industries refer these relations when installing the solar panel [72,74].

Armstrong and Hurley proposed a methodology that can be applied appropriately in locations with low clearness index. It required latitude angle, monthly sunshine hours and hourly cloud data. Reindl correlation is used to calculate diffuse and direct radiation component for partly cloudy and overcast days before applying the Perez model. The tilt angle varies from 0° to 90° in steps of 1° and the maximum solar radiation on solar panel is

**Table 5**  
Tilt angle by latitude angle.

Author	Tilt angle	Application
Duffie and Beckman [92]	$(\theta + 15^\circ) \pm 15^\circ$	These methods are used for calculating approximate tilt angles in different latitudes. The minus sign is refers to summer and the positive sign for winter.
Heywood [93]	$\theta - 10^\circ$	
Lunde [94]	$\theta \pm 15^\circ$	
Chinnery [95]	$\theta + 10^\circ$	
Lof and Tybout [96]	$\theta + (10^\circ \rightarrow 30^\circ)$	
Garg [97]	$\theta + 15^\circ, \theta - 150^\circ, 0.9\theta$	

chosen for optimum condition. The researchers use to compare this methodology with Elsayed's correlation and found the methodology is better for utilizing overcast days. It can be noted that Elsayed's correlation gives accurate results in clear sky condition as well [74]. Yadav and Chandel reviewed others methods for optimizing tilt angle which included Genetic Algorithm (GA), Simulated Annealing (SA), Particle Swarm Optimization (PSO) and Artificial Neural Network techniques (ANN) [72].

#### 4.1.5. Electrode materials

Selection of electrode material is depends on the type of wastewater. Aluminum and iron materials are generally used for treating textile wastewater since they are capable to produce in-situ coagulant or Fenton reagent to remove the dye compounds [56,58]. Other common materials are stainless steel, carbon felt, graphite, DSA-O<sub>2</sub>, boron doped diamond (BDD) and bismuth-doped titanium dioxide (BiO<sub>x</sub>-TiO<sub>2</sub>). Carbon based materials are cheaper but difficult to apply in large-scale processes due to their brittleness, bulky nature in addition with high electrical resistivity [75]. BDD is considered as an excellent material in electrochemical process since it has very high over potential for oxygen and hydrogen evolution. Hence, this material produces a wide electrochemical potential window which enables to electro-analyze different types of chemical species [76,77]. However, BDD it is very expensive and for this reason they have limited usage [78]. Dimensionally stable anode (DSA) is an inert metal coated with noble metal oxides such as IrO<sub>2</sub>. They have a long life span due to their inertness and higher corrosion resistance [79].

#### 4.1.6. Shape and arrangement of electrode

The shape and arrangements of electrodes within a cell is another important parameter for affecting the power generation. Plane parallel electrodes are the most popular configuration because it provides uniform current distribution in the system. Mesh or reticulated planes are also used to increase the contact area. Porous electrode has different reaction zones since there is a potential profile along the electric field. Hence, a methodology is required to control the applied current for achieving approximately 100% current efficiency [80]. Moreover, porous electrodes could provide a large active specific surface area and high mass transfer coefficients [81]. Researchers demonstrated the effect of a cation membrane inserted between anode and cathode compartments to prevent the mixing of anolyte and catholyte and allow certain ions to pass through to the cathode side for further reactions [56,82]. However, fouling problem is the main issue for membrane usage and increases complexity in the operations [7]. Table 6 presents various PV electrochemical systems designed for wastewater treatment process.

### 5. Performance of PV electrochemical system

A few researchers investigated PV electrooxidation and electroreduction systems for treating wastewater having high organics

concentrations with the generation of hydrogen gas. This is one of the green technology approaches to generate hydrogen, since most of industrial scale hydrogen production is carried out through steam-methane reformation (SMR) at high temperatures. In addition, SMR method is associated with high emissions of carbon oxides. So far, a method of hydrogen generation through water electrolysis is less popular as it is also associated with high energy and cost [57,83,84]. In this regard, PV system is a promising alternative method to provide electrical power in hydrogen production. Navarro-Solís et al. (2010) demonstrated H<sub>2</sub> production as a byproduct of synthetic textile effluent treatment. Effect of different electrode materials (stainless steel and carbon steel), applied electric potential ( $\Delta E_{cell}$ ) and supporting electrolyte were investigated for hydrogen production. H<sub>2</sub> was generated at the cathodic side; whereas decolorization of synthetic dye wastewater was occurred at the anodic side through oxidation by iron ions produced by the sacrificial Fe-anode that reacted with H<sub>2</sub>O<sub>2</sub> to form Fenton's reagent. The anodic and cathodic compartments were separated by a cation permeable membrane. The complete oxidation of dye wastewater is a fast process and H<sub>2</sub> production allowed its conversion into electrical energy to decrease overall energy consumption [56].

A hybrid PV electrochemical reactor was developed by Park et al. (2008) to generate molecular hydrogen at the stainless steel cathode and to oxidize organic substrate at the titanium anode coated with BiO<sub>x</sub>-TiO<sub>2</sub>. A commercial amorphous silicon PV panel with power rating of 6.4 W and active surface area of 1280 cm<sup>2</sup> was connected to the electrodes to supply the voltage and current to the system. Hydrogen production rate at the cathode was influenced by anodic oxidation of organic substrate, where it was seen that the energy efficiency was increased about 53% for H<sub>2</sub> generation at neutral pH [57]. Fikret Kargi (2011) also investigated the hydrogen gas generation from electro-hydrolysis of organic compounds present in industrial wastewater by using electrical power produced by PV system. Three types of electrodes (graphite, stainless steel and aluminum) having diameter of 0.9 cm and length of 49.5 cm were used, and the total hydrogen production was compared. Aluminum electrodes gave the highest accumulative hydrogen gas evolution. It was concluded that the system is fast and energy efficient to produce hydrogen gas and to remove organic compounds from the wastewater simultaneously [85].

Another hybrid photovoltaic electrochemical system was used to treat urea and urine which is capable to produce hydrogen gas simultaneously. BiO<sub>x</sub>-TiO<sub>2</sub> and stainless steel were used as anode and cathode material respectively. Three different electrolytes namely NaCl, LiClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> were used to investigate the efficiency of the system. LiClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> electrolytes showed the lowest reduction of urea and no hydrogen gas was produced. NaCl electrolytes showed great results mostly due to the crucial role of chloride ions. During chloride electrolysis, different types of active chlorine species such as Cl<sub>2</sub>, HOCl and OCl<sup>-</sup> were formed at anodic side and they were electrochemically reduced at the cathode. The urea was oxidized by active chlorine species to form carbon dioxide, ammonia and nitrate as final products. Active chlorine species also increased the quantity of hydrogen production. The electrolysis of urine was successful to generate H<sub>2</sub> even in the absence of added electrolytes since sufficient amount of chloride and other ionic species are originally present in the urine [86].

Dominguez-Ramos et al. (2010) designed a single compartment electrochemical reactor where boron-doped diamond anode and cathode were placed in parallel configuration having 1 mm of inter-electrode gap to remove the organic materials from a lignosulfonate solution. Four of monocrystalline photovoltaic modules were connected to give a total peak power of 640W. The solar panel was installed on the roof of ETSIlyT, University of Cantabria (W3°47'52.17", N43°28'22.33") tilted at 38° at the

**Table 6**

Wastewater treatment process setup powered by PV.

Electrode shape	Anode	Cathode	Surface area		Electrochemical cell configuration	PV module installation characteristic	Ref.
			Anode	Cathode			
Mesh	Stainless steel, carbon steel	Stainless steel, carbon steel	420 cm <sup>2</sup>	420 cm <sup>2</sup>	Anodic and cathodic chamber is separated with a cation permeable membrane	Model BP 350 U with 50 W	[56]
–	BiO <sub>x</sub> -TiO <sub>2</sub> coated titanium	Stainless steel	–	–	Single compartment	Amorphous silicon module with 6.4 W	[57]
Rod	Stainless steel, aluminum, graphite	Stainless steel, aluminum, graphite	–	–	Single compartment	115 W PV module	[85]
Plane	BiO <sub>x</sub> -TiO <sub>2</sub>	Stainless steel	6 cm <sup>2</sup>	6 cm <sup>2</sup>	Single compartment	–	[86]
Plane	BDD	BDD	Total wet area is 70 cm <sup>2</sup>	Total wet area is 70 cm <sup>2</sup>	Single compartment	4 × monocrystalline modules with 160 W	[61]
–	Aluminum	Stainless steel	–	–	Central anode between two cathodes	Tilted at 38° South oriented (20°W)	[60]
Plane	DSA-O <sub>2</sub>	Carbon felt	3300 cm <sup>2</sup>	3300 cm <sup>2</sup>	Single and bipolar cell	Poly-crystalline silicon with 38.4 W Tilt at 55° South oriented (0.4°W)	[71]
Reticulated	Stainless steel	carbon	25 cm <sup>2</sup>	25 cm <sup>2</sup>	Anodic and cathodic chamber is separated with a cation permeable membrane	40 × polycrystalline silicon modules with 38.48 W are connected in parallel or series Tilt at 55° South oriented (0.4°W)	[82]
						Model BP 350U with 50W purchased from Syscom Inc.	

southern orientation (20°W). There was no shadowing effect during the experiments. The PV modules were directly connected to the electrochemical reactor through a fuse box. It was found that PV electrooxidation provided removal of 90% of TOC in 240 minutes and it greatly depended on the electrode area and photovoltaic module area [59].

Valero et al. (2008) constructed a PV electrocoagulation reactor to remove dyes from the synthetic textile wastewater. A central aluminum anode was placed in between two stainless steel cathodes and total anodic area was 235 cm<sup>2</sup>. A PV module made from poly-crystalline silicon with a peak power of 38.4W was installed facing to the south (0.4°W) at University of Alicante (38.3877°N, 0.5186°W) with a tilt of 55°. The highest decolorization efficiency was reached up to 98.1% when the current density and flow rate were 17 mA/cm<sup>2</sup> and 2 L/h respectively. The research verified that the PV array configuration depends on the instantaneous solar irradiation and its rearrangement is important to maintain the capacity of power generation [58]. Valero et al. (2010) repeated the work by replacing the anode and cathode with DSA-O<sub>2</sub> and carbon felt respectively. The reactor was a divided filter-press with a cation exchange membrane and 40 PV modules were connected in parallel or 2 stacks were connected in series (20 modules in parallel per stack). The objectives were to compare the dye degradation efficiency by using conventional electric power source and PV electrocoagulation system, and the effect of PV configuration on dye removal efficiency. The results showed that decolorization of dye compounds by using PV-electrocoagulation can be successfully carried out at various atmospheric conditions (sunny and partly clouded). It was again confirmed that the optimum PV array configuration was influenced by the solar irradiation intensity, conductivity of the solution and pollutants concentration [71].

Figueroa et al. (2009) studied decolorization of textile wastewater by using the Fenton's reagent. It was demonstrated that Fenton's reagent can be produced at a lower cost through oxygen reduction on the cathode of the PV system. A perforated plane shaped carbon with 60 pores per square inch was used as cathode and stainless steel gauze having 25 cm<sup>2</sup> area was utilized as anode material. The effect of electrolyte nature, its concentration, current density and rate of Fenton's reagent electro-production were

investigated. The results showed that textile effluent compounds can be effectively oxidized at pH 2.8 in 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution. Higher removal efficiency was expected by changing the anode material to iron electrode [82].

The discussed study on the applications of electrochemical methods coupled with PV technology provides *in-situ* electric energy for the treatment of water and wastewater. Further development and improvement of PV technology is an ongoing progressive expansion covering numerous countries worldwide with serious interest to invest in and benefit from renewable solar energy generation.

## 6. Conclusion

Electrochemical methods are well accepted for efficient destruction of various environmental pollutants. However, combination of electrochemical methods with PV solar cell is a novel technological approach to enhance the sustainability of wastewater treatment processes. Installation of PV technology is especially beneficial for tropical and subtropical countries. To date, many research studies successfully demonstrated the applicability of PV electrochemical systems for the treatment of textile wastewater and production of hydrogen gas. The significant operating variables are the light absorbance capacity of the material, PV array configuration, tilt angle, electrode materials, their shape, number and arrangement. However, there is a gap in researches for installing PV system in real wastewater treatment and hence more work is encouraged in this area. Studies on saving the utility cost by using PV electrochemical system for treating different wastewater could a new scope for research.

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